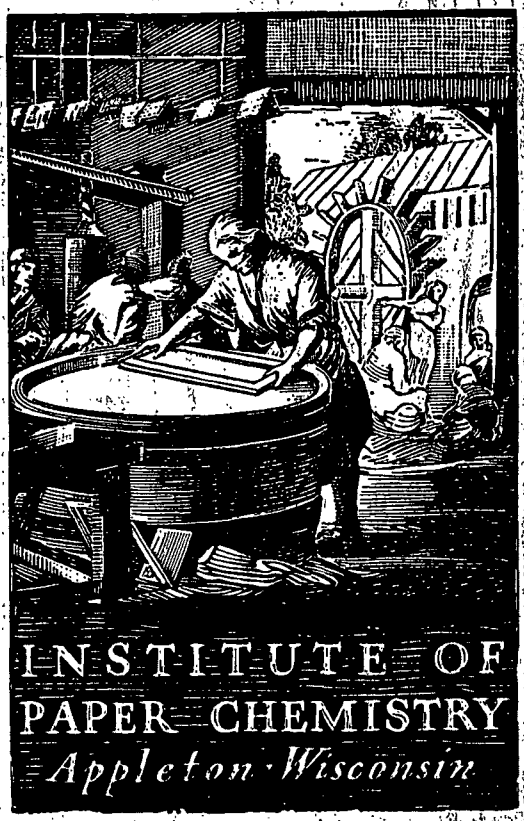

INCREASED YIELDS IN ALKALINE PULPING. II. A STUDY OF OPTIMUM CONDITIONS FOR USE OF ADDITIVES IN THE PREVENTION OF PEELING

Project 2942

Report Seven

A Progress Report

to

MEMBERS OF GROUP PROJECT 2942

May 21, 1975

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

INCREASED YIELDS IN ALKALINE PULPING. II. A STUDY OF OPTIMUM CONDITIONS FOR USE OF ADDITIVES IN THE PREVENTION OF PEELING

SUMMARY

The stopping reaction, occurring with aqueous sodium hydroxide and cellodextrins, has been found to occur to the same extent at 120°C as at lower temperatures. Also experiments at 90°C show that sulfidity has no effect on the stopping reaction.

Analysis for the stopping reaction depends on a completion of the peeling reaction and a determination of the remaining alkali-stable glucosidic bonds. Experiments with cellobiose have shown that the kinetics of the peeling reaction is linear down to 99% reaction, so presumably the reaction is not slowed up by reaction products, and goes readily to completion.

Attempts to isolate one or more stopping acids, from reaction of alkali with either cellobiose or cellodextrins, have been unsuccessful. This may be due to the very small amount of product available.

Reactions of cellobiose with polysulfide solutions show appreciable amounts of disaccharide acids, formed by oxidation of the end units; these acids can be readily shown on the gas chromatograph. This oxidation, while much faster than the stopping reaction, is much slower than the peeling reaction. Thus, the yield of these acids, in orange liquor, a mixture of sodium polysulfide and sodium hydroxide, is much less, because of the competitive peeling by sodium hydroxide.

The yields of disaccharide acids formed in orange liquor do not vary with temperature (90 to 150°C) and these compounds seem to be fairly stable to both alkali and to polysulfide solution.

The polysulfide content of the orange liquor decreased quite rapidly in two to ten minutes at 150°C, but was quite constant at 90°C.

The presence of very small amounts of oxygen (as dissolved air) in the alkaline solutions and its possible effect on the stopping reaction is discussed.

INTRODUCTION

Originally this project, in its second stage, had a program which included the use of various additives to prevent the peeling reaction. At a meeting of the cooperators in April 1974 it was decided that the program should concentrate on the stopping reaction, and that no further work should be done on the use of additives. Also, it was decided that some work should be done on the extent of peeling in sodium polysulfide solutions.

Since that time the stopping reaction, occurring in homogeneous alkaline solutions of cellobiose and cellodextrins, has been studied at temperatures ranging from 75°C to 120°C. The work is summarized in this report. The reaction was also studied in white liquor to check the effect of sulfidity.

A discussion of the validity of our analysis for the stopping reaction is presented. The peeling process must be complete before the remaining alkali-stable material can be analyzed. The ratio of stopping, relative to peeling, is also discussed in relation to data obtained by other workers with polysaccharides.

Attempts were made to isolate the stopping acids, presumably formed in the alkaline systems, and reasons for lack of success in this area are discussed.

A series of reactions was run with polysulfide solutions and cellobiose to show the effect of temperature on the reaction, and also the competition of alkali in orange liquor with the oxidative activity of the free sulfur. Also the decomposition of polysulfide solutions at short reaction times was studied in the flow reactor.

This is the final report on this project, and several ideas for future work in this area are given.

THE ALKALINE STOPPING REACTION

BACKGROUND

In Report Six a detailed discussion of peeling and stopping was given. Part of this discussion is repeated below, for the benefit of the reader and to add coherence to this report. In the present section reference is often made to the alkaline stopping reaction, a rearrangement of the end unit, in contrast to the polysulfide stopping reaction, where the end unit is oxidized.

The major reaction occurring in the alkaline degradation of oligo- and polysaccharides is peeling, the rapid splitting off of end groups as isosaccharinic acid. This is shown in Fig. 1a and 1b. If the peeling reaction is carried to completion, the final unit, glucose, is isomerized to glucometasaccharinic acid (Fig. 1c). Thus, one would expect a large amount of isosaccharinic acid and a small amount of the meta acid when n is large. This is shown in Fig. 2, a gas chromatographic curve for products from a cellodextrin, where n = 6. The large peak for isosaccharinic acid has a retention time of about 750 seconds; the smaller peak at 900 seconds is the glucometasaccharinic acid. The multiple character of the peaks is probably due to the presence of α- and β-isomers, and also to the presence of a mixture of straight chain acids and lactones[1]. In cellobiose, where n = 1, one would expect equal amounts of the iso- and meta-acids, and the chromatographic curve (Fig. 3) bears this out. Finally, the absence of any isosaccharinic acid is shown in Fig. 4, a chromatographic curve for glucose.

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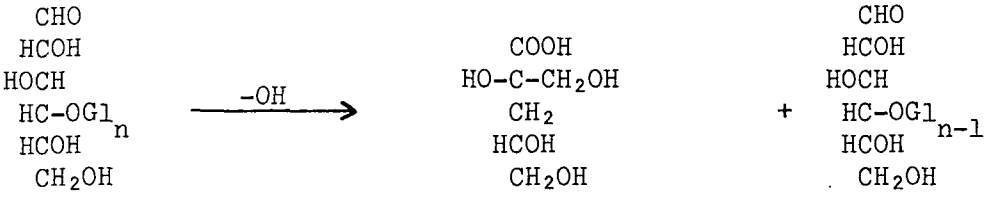
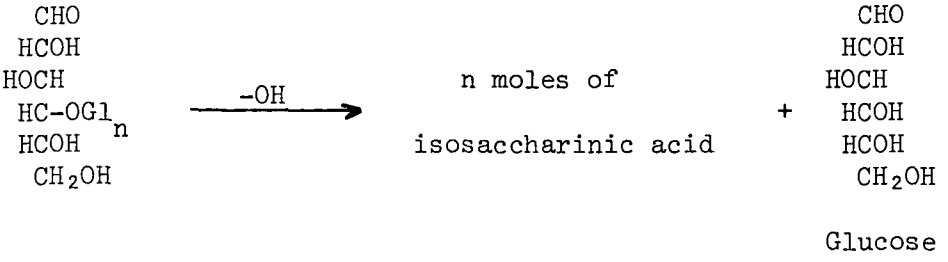
[1]The α- and β-isomers differ in the optical configuration of the carbon atom adjacent to the carboxyl group; this can be seen in Fig. 1a and 1c.

(a)



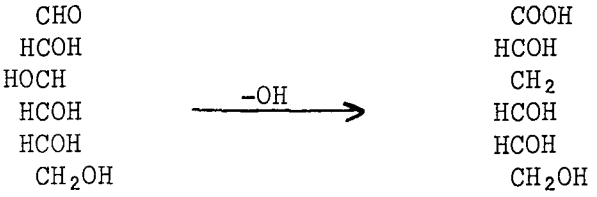
Isosaccharinic Acid

(b)



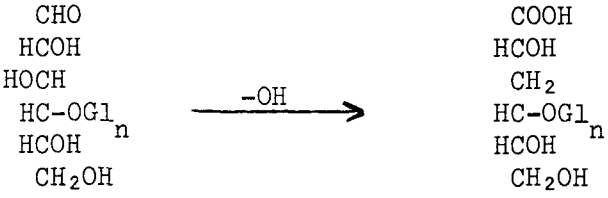
Glucose

(c)



Gluco-metasaccharinic Acid

(d)



Glucosyl-metasaccharinic Acid (GMS) (n = 1)
or
Cellodextrin-metasaccharinic Acid (DMS) (n > 1)

(e)

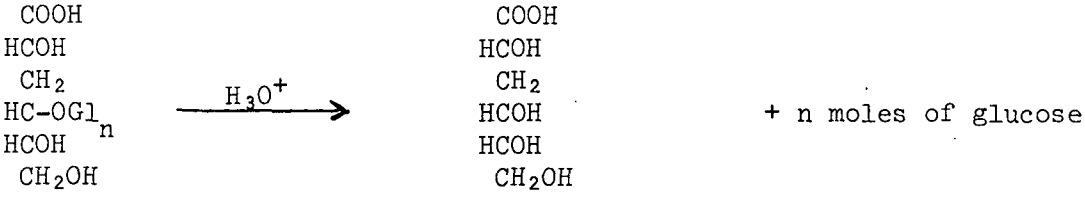


Figure 1. Reactions Occurring in the Peeling and Stopping Reaction of an Oligosaccharide; also Hydrolysis of GMS

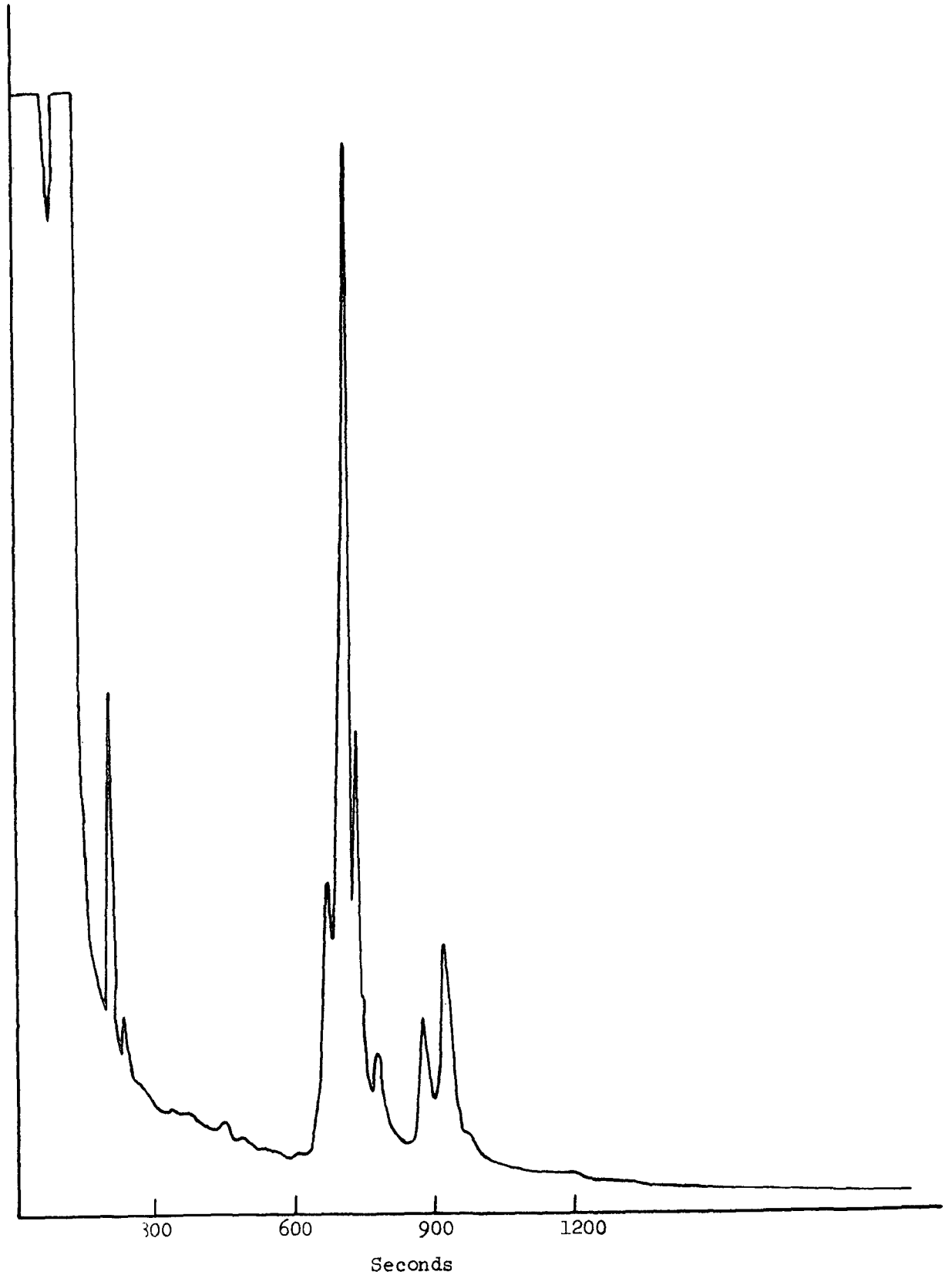


Figure 2. Degradation Products from Cellodextrin, 1 hour in 2N NaOH at 90°C, Showing Predominance of Isosaccharinic Acid. Trimethylsilyl Derivatives on OV-17 Column, 6 ft x 1/8 Inch, Programmed 130 to 200°C, at 2°/minute

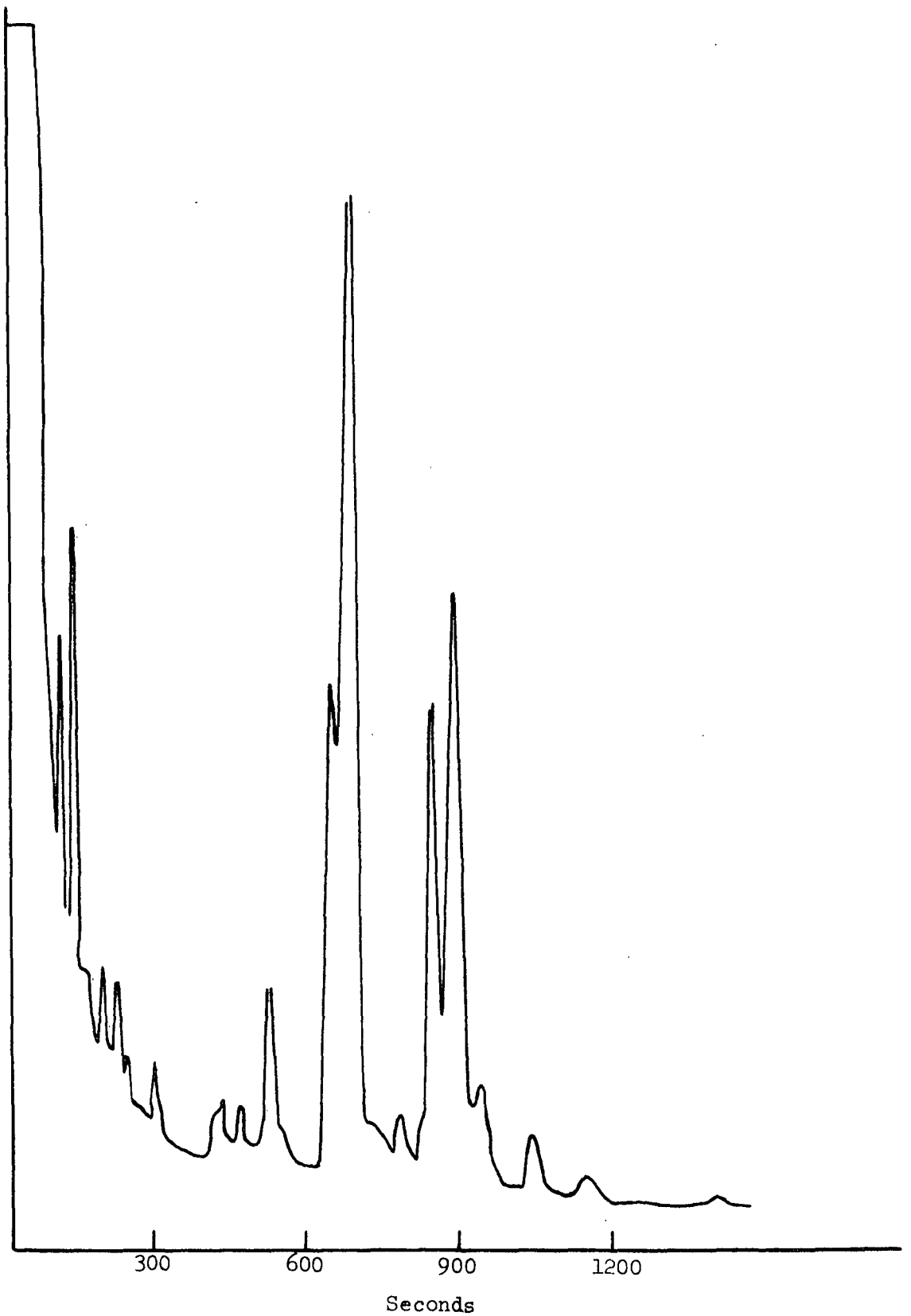


Figure 3. Degradation Products of Cellobiose After 1 hour in 2N NaOH at 75°C; Gas Chromatographic Curve on OV-17 Column, 6 ft x 1/8 Inch, Programmed 130 to 200°C, at 2°/minute

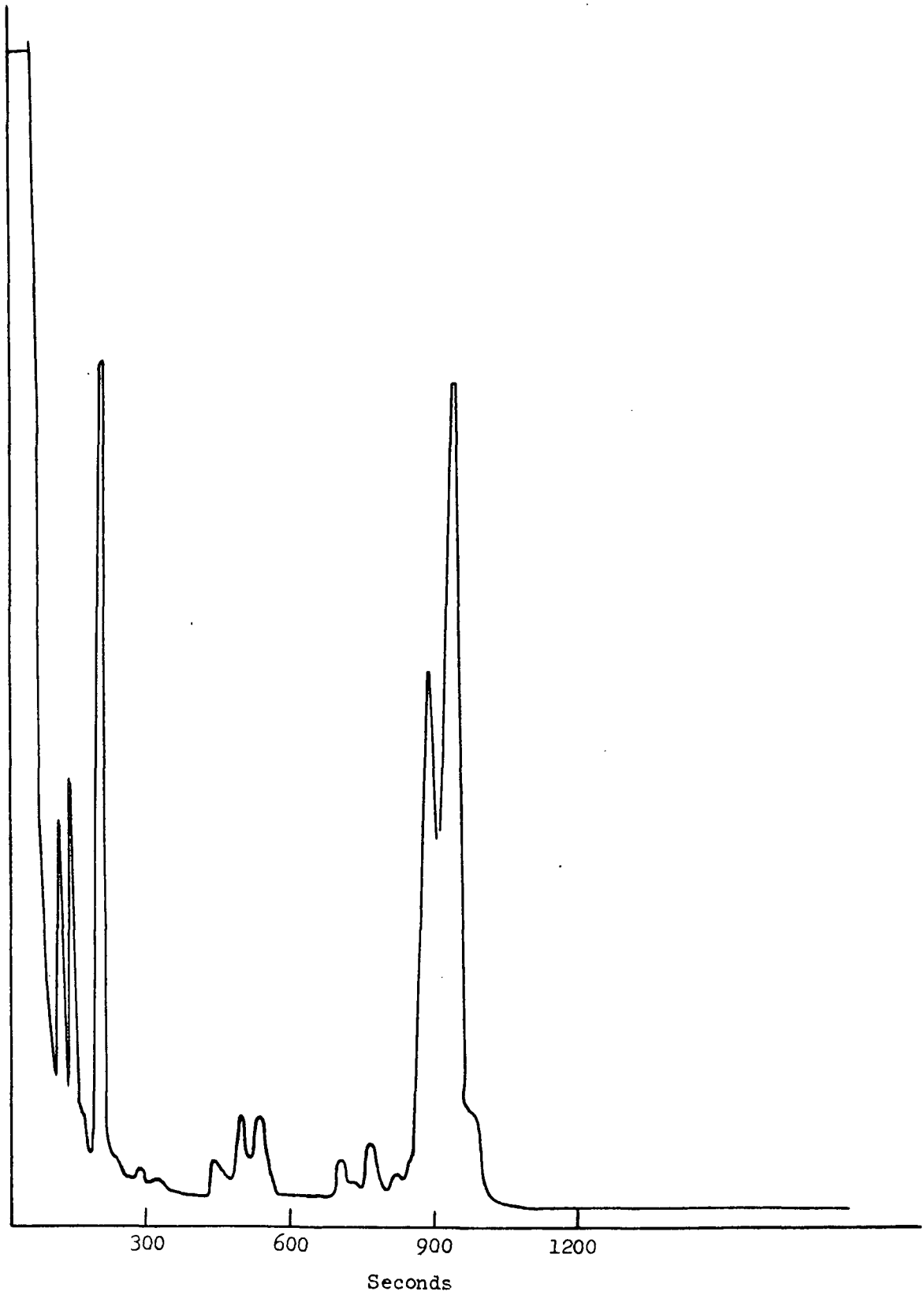


Figure 4. Degradation Products of Glucose; 1 hour in 2N NaOH at 90°C, Gas Chromatographic Curve; OV-17 Column, 6 ft x 1/8 Inch, Programmed 130 to 200°C and 2°/minute. Trimethylsilyl Derivatives

The minor reaction occurring in the alkaline degradation of oligosaccharides and polysaccharides is the stopping reaction, the rearrangement of the end unit to a metasaccharinic acid, without the breakage of a glucosidic bond (Fig. 1d). Such units are relatively stable to further alkaline attack; there is no peeling reaction for these compounds, and the glucosidic bond is broken very slowly by alkali or more rapidly by acid hydrolysis (Fig. 1e). Such a stopping reaction will then lead to the formation of alkali-stable polysaccharides, a desirable product in pulping reactions.

The acid hydrolysis of such a glucosyl-metasaccharinic acid[2] (GMS) or a cellodextrin-metasaccharinic acid (DMS) (Fig. 1e) will give one mole of meta-acid and n moles of glucose. If the peeling reaction is carried to completion, the accompanying stopping reaction can be identified by the liberation of glucose by such an acid hydrolysis. The reaction mixture will then consist of a small amount of glucose and a large amount of various saccharinic acids. Such a system is shown in Fig. 5, where the α-glucose peak is fused into the two peaks representing the gluco-metasaccharinic acid[3].

An analytical scheme for the stopping reaction then involves several steps: (1) carrying the peeling reaction to completion, (2) hydrolysis of the small amount of GMS or DMS present, (3) separation of the resulting glucose from the various saccharinic acids, and (4) quantitative analysis of the glucose. This we have done in this project, with the aid of ion-exchange resins in Step (3) and gas chromatography of the trimethylsilyl derivatives in Step (4). The details of this method were described in Report Six.

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[2]This GMS, a C_{12} acid containing a glucosidic bond, should not be confused by the reader with gluco-metasaccharinic acid, a C_6 acid. Please refer to Fig. 1d and 1e for the formulae for the two compounds.

[3]Trimethylsilylation of glucose, where the latter is obtained by concentration of an aqueous solution, will give two peaks, of roughly equal size, for the two anomers, α- and β-glucose.

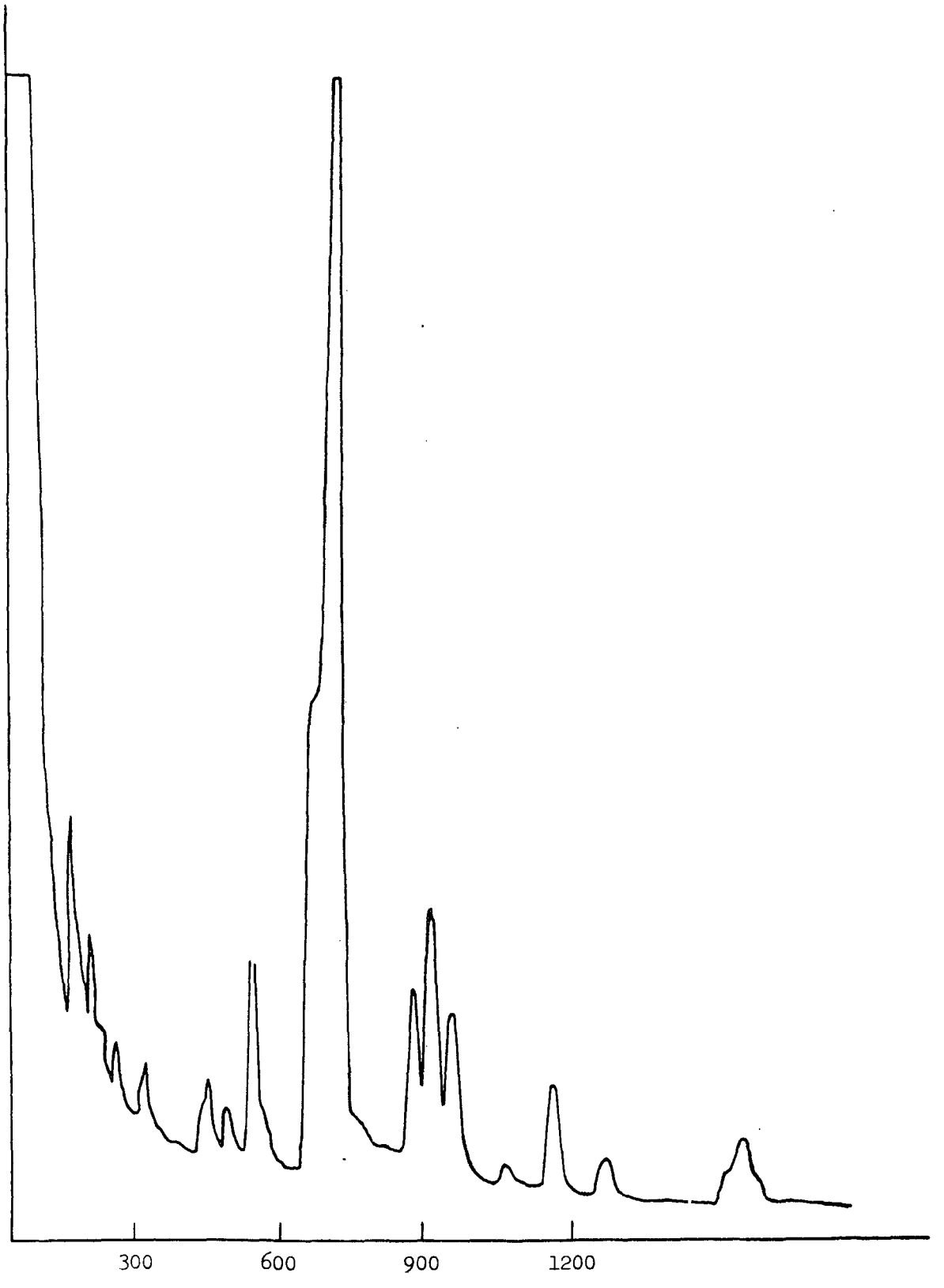

Figure 5. Hydrolyzate of Cellodextrin Reaction Products, Showing Glucose Proximity to Metasaccharinic Acid Peaks. Gas Chromatographic Curve of Trimethylsilyl Derivatives, on OV-17 Column, 6 ft x 1/8 Inch, 130 to 200°C, at 2°/minute

The reactions presented in Fig. 1a to 1d are the major reactions occurring in an alkaline system. However, fragmentation of sugar units may occur, and many small peaks appear in the gas chromatographic curves. This fragmentation occurs especially in the degradation of glucose, to give products such as lactic acid, a C_3-acid, and C_4- and C_5-metasaccharinic acids. Peaks representing such products are shown in Fig. 6.

In the present work we have used primarily an oligosaccharide, a cellodextrin mixture with an average DP = 7. The advantage of such a starting material is that the resulting DMS, when hydrolyzed, will give a large amount of glucose, in contrast to the GMS derived from cellobiose. The analysis of the latter system is more difficult, a matter of analyzing for a "needle in a haystack."

EXPERIMENTAL RESULTS

In the last report data were given for the alkaline stopping reaction at 75°C and at 90°C in aqueous alkali. Since then reactions have been run at 120°C in alkali and at 90°C in a white liquor to check the effect of sulfidity. The data for all of these experiments are summarized in Table I.

The main conclusion to be drawn from these experiments is that the ratio of peeling to stopping is not affected by temperature, and sulfidity does not have an effect either. The tendency for a glucose end unit on a cellodextrin to either split off (peel) or to rearrange into an alkali-stable unit (stopping) seems to be an inherent property of the unit, and the two reactions bear a constant ratio to each other, which is unaffected by temperature. There is some scatter in the data; the analysis for small amounts of glucose after hydrolysis is not very precise. However, the ratio of peeling to stopping

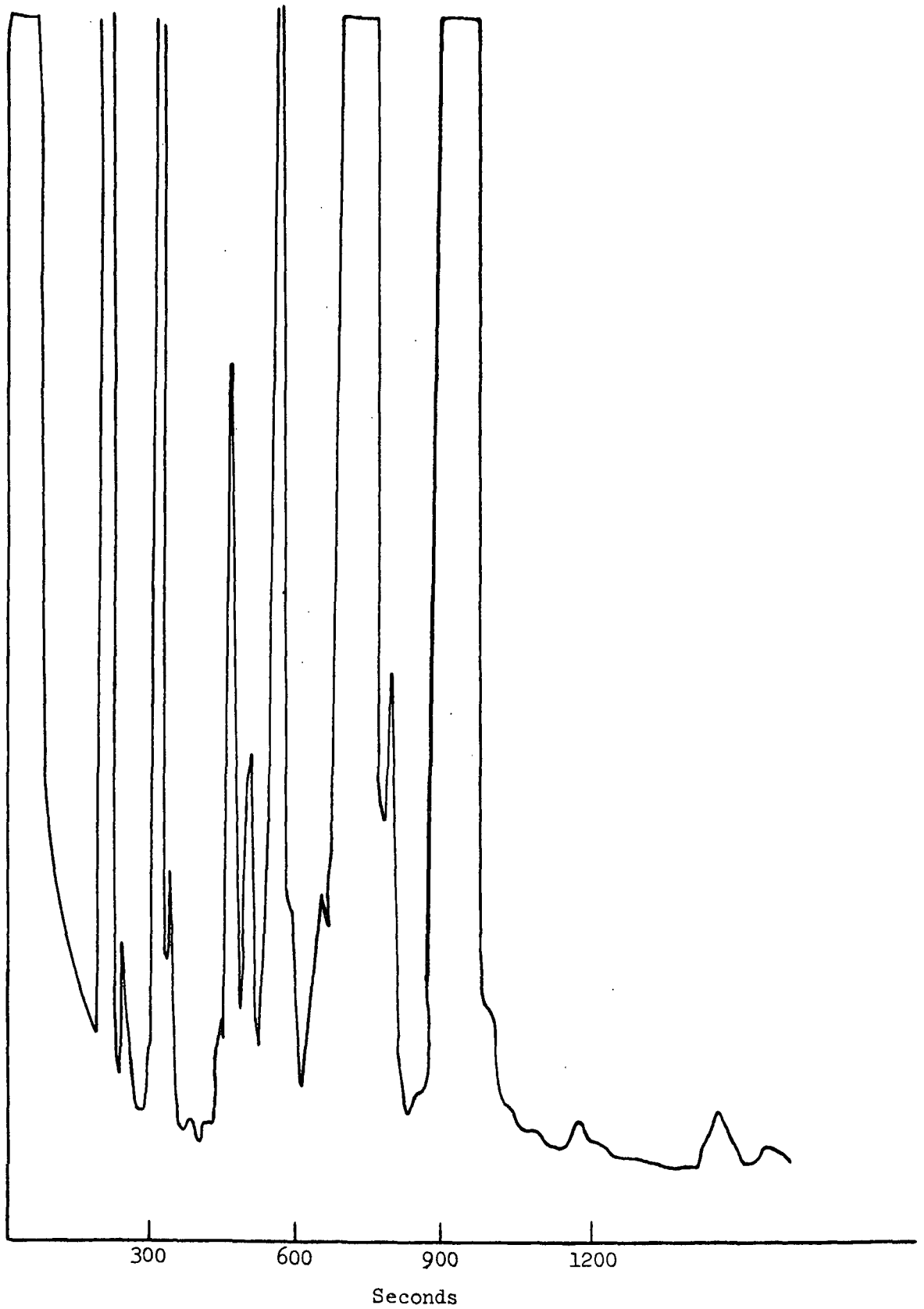

Figure 6. Degradation Products from Cellodextrin, 1 hour in 2N NaOH at 90°C, Gas Chromatographic Curve at High Sensitivity, Trimethylsilyl Derivatives on OV-17 Column, 6 ft x 1/8 Inch, 130 to 200°C, at 2°/minute

TABLE I

YIELD OF GLUCOSE FROM HYDROLYSIS OF ALKALI-DEGRADED OLIGOSACCHARIDES

Starting Material DP	Temp., °C	Time, hr	Liquor Composition, g/l NaOH	Liquor Composition, g/l Na_2S	Glucose Yield, Based on Starting Material, %	Stopping, Relative to Peeling, %	Ratio of Peeling to Stopping
7	75	1	80	0	2.0	0.67	150
	75	2	80	0	2.3	0.77	130
	75	4	80	0	0.96	0.32	310
	75	16	80	0	1.65	0.55	180
7	90	4	80	0	1.12	0.37	270
	90	4	40	0	1.10	0.37	270
	90	4	28	11.7	1.25	0.42	240
2	90	4	80	0	0.19	0.19	530
7	120	0.3	80	0	1.74	0.58	175
	120	1	80	0	1.58	0.53	190
Large[a] (hydrocellulose)	65		50	0		0.1	1000
	78		50				371
	87		50				477
	100		50				292
	100		50				294
	132		50				248
	132		50				222

[a]The hydrocellulose data are those of Haas *et al.* (1); the data at 75°C and the first and fourth experiments at 90°C were given previously in Report Six.

ranges from 175 to 310, and this ratio compares favorably with data obtained by Haas, Hrutfiord and Sarkanen (1) on a polysaccharide, a hydrocellulose. These workers do show a decrease in this ratio with increasing temperature; however their data represent a heterogeneous system, and their ratios represent the reactions occurring in the accessible or noncrystalline portions of the polysaccharide. In their system only a relatively small portion of the substrate was involved in the peeling and stopping; they determined rate constants k_1 and k_2 for the two reactions, and the ratios given in Table I are the ratios of those two constants. They also determined a second stopping rate constant, k_{cr}, which represented the inaccessibility of part of the polysaccharide to attack by alkali, that part in the crystalline regions. This k_{cr} ranges from two to ten times the magnitude of the k_2 stopping constant, and this showed that the bulk of the polysaccharide molecule was physically protected from alkaline attack. Because of this k_{cr} factor, the bulk of a polysaccharide molecule, in a heterogeneous alkaline system, survives the peeling process, and this surviving fraction is made up of two parts, a chemically stopped region and a physically stopped (or inaccessible) region.

Because the chemical stopping reaction is only a part of the total stopping reaction, the final yield of a pulp is affected only to a minor extent by this end-group rearrangement. According to the data of Haas, et al. (1) at lower temperatures the physical stopping reaction is more favorable, and so this is a good opportunity, in the heat-up period of a cook, for alkali-stable polysaccharides to accumulate.

The data for the cellodextrins at the several temperatures show a bit of scatter and it is difficult to determine if there is any trend of the ratio of peeling to stopping with temperature. As the reaction temperature was raised,

the time was shortened; a large number of experiments will be needed, at various times, to ascertain whether the alkali-stable bonds are being degraded slowly. The two reaction times at 120°C tend to bear this out, but more data are needed to demonstrate this more firmly.

The sulfidity experiment at 90°C shows that the stopping reaction is controlled by the hydroxyl ions, an attack by base, and that the effect of sulfide or hydrosulfide ions, which are strong nucleophiles, is not evident. This result agrees with the data found earlier (Report Six) showing the rate of peeling to be unaffected by sulfidity also.

VALIDITY OF THE ANALYSIS FOR THE STOPPING REACTION

As mentioned in Report Six, we have been concerned about our method of determining the stopping reaction with either cellobiose or with oligosaccharides. This method consists of carrying the peeling reaction to completion, hydrolyzing the reaction products, and determining the amount of glucose liberated in this hydrolysis. The glucose thus found has been attributed to alkali-stable glucosidic bonds formed in the stopping reaction, bonds that are resistant to peeling.

Below are listed several arguments for the validity of this method, and also several bits of nonsupporting evidence. The latter disturb us a bit but we do believe the method is valid. Because of time limitations we have not been able to clear up the negative aspects, but we do believe this can be done.

1. Leveling off of the glucose yield with time. As shown in Table I, the amount of glucose found is constant, and within experimental error does not

change with time. If any unpeeled substrate were present, a higher glucose yield would be obtained. The glucose values found do not change, within experimental error, on further heating with alkali.

2. Time needed for completion of the peeling process. Before an analysis is carried out for the stopping reaction, all the end groups must have either peeled or have been stopped, rearranging to nonpeeling units. For a calculated time necessary to do this, we have used as a theoretical minimum time a period equal to ten times the half life of the starting material. For cellobiose this half life has been determined for several temperatues (see Report Four) and theoretically the tenfold period should lead to only 0.1% of the starting material. For oligosaccharides, with a series of consecutive reactions leading to intermediates of lower degree of polymerization, we have calculated the necessary times (see Report Six, Fig. 7 and Table III). This time, for an oligosaccharide of DP = 7, is 3 times that required for a disaccharide, with DP = 2.

These two times, ten half-lives and thirty half-lives, are based on two assumptions. One is that the reactions continue for very long times with the same rate constants; in other words the products do not interfere with the kinetic behavior of any unaltered starting material. The second assumption is that all of the end units of the oligosaccharides peel at the same rate, regardless of DP. In other words, the time required for an oligosaccharide of DP = 7 to peel to DP = 6 should be the same as for cellobiose (DP = 2) to peel to DP = 1 (glucose).

We cannot check the second assumption very easily in the laboratory, but we have checked the first assumption for cellobiose (see Fig. 7 and 8) in 1-2N NaOH at 120°C; the half-life for this reaction was approximately 2 seconds

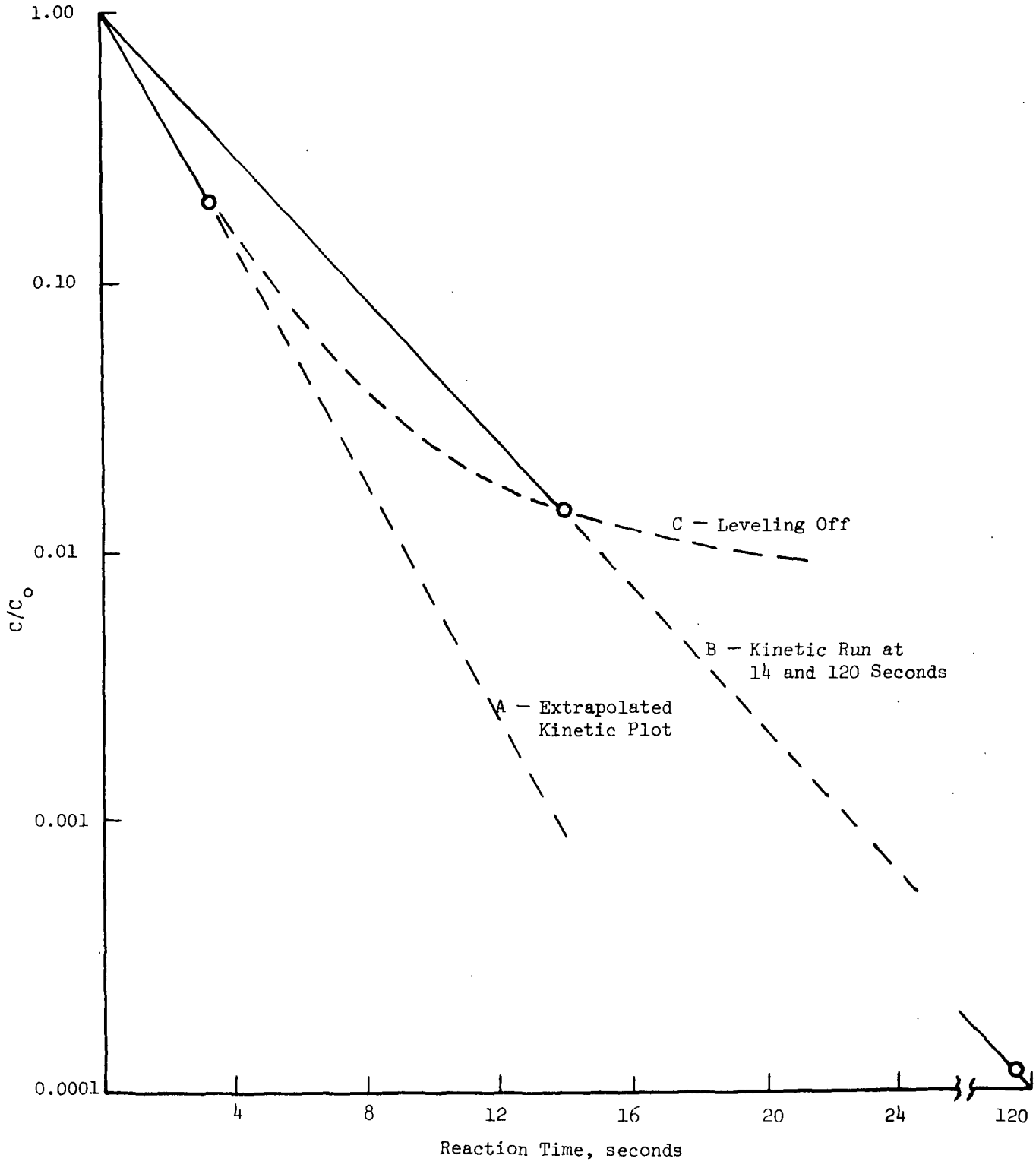

Figure 7. First Order Kinetic Plot of Disappearance of Disaccharides in the Reaction of Cellobiose with 1-2N NaOH at 120°C

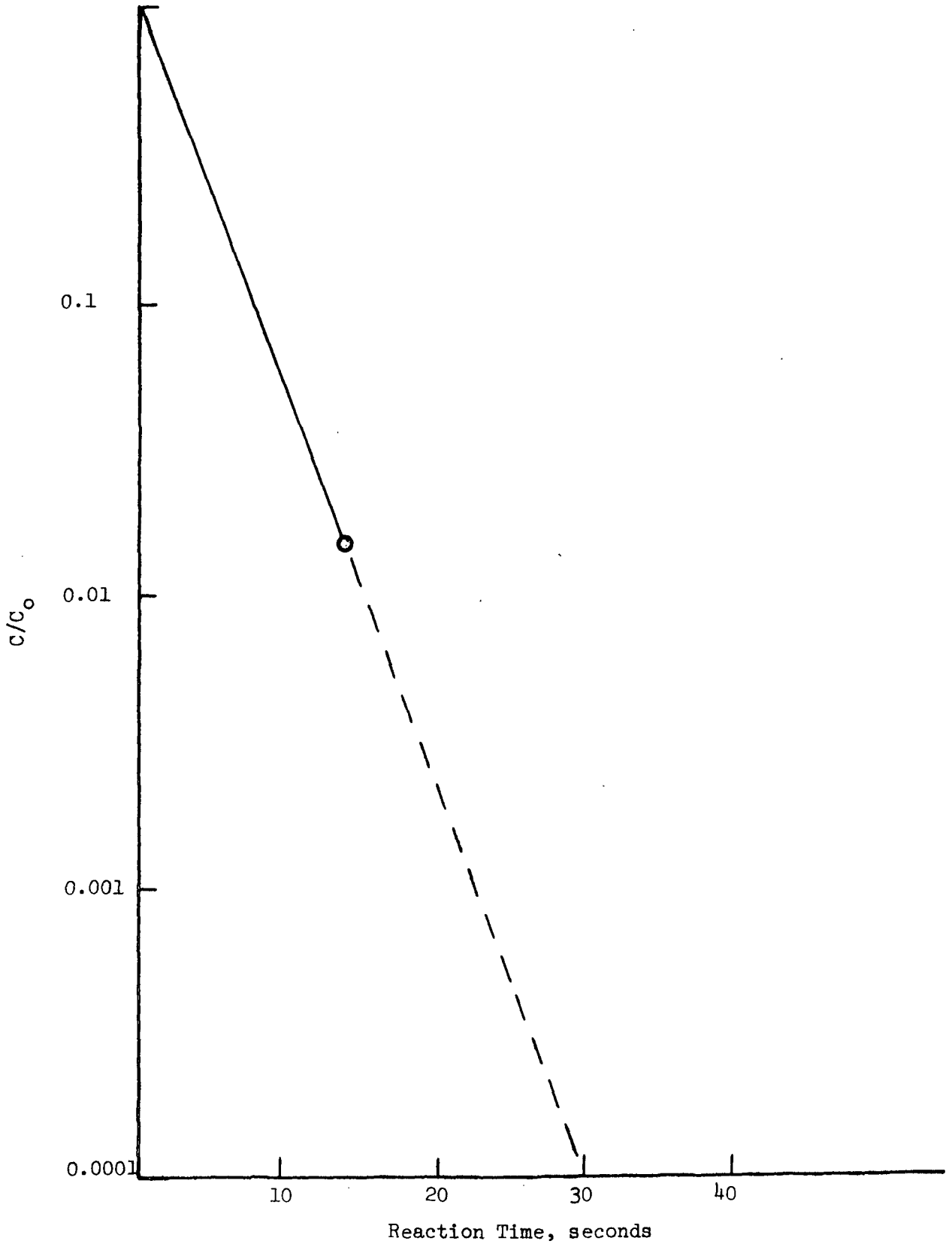

Figure 8. First Order Kinetic Plot of Disappearance of Cellobiose in its Reaction with 2N NaOH at 120°C

(see Report Four, Fig. 7). A semilog plot for the pseudo-unimolecular rate expression is approximately linear down to 1.5% of unreacted starting material. Below this value we have difficulty in analysis. At 14 seconds reaction time in the flow reactor we found 1.5% cellobiose remaining and the gas chromatogram of this is shown in Fig. 9. When the reaction was carried out for two minutes, no trace of cellobiose could be detected on the gas chromatograph.

If we use the reaction time of 14 seconds as 7 half-lives, then the theoretical amount of starting material left should be 1/128 or 0.78%; the found value is about twice this. Very few rate studies are carried out beyond 90% reaction, so the plots shown in Fig. 7 and 8 represent extreme cases, and the extrapolations are carried out beyond the limits of our analysis.

Figure 7 shows a plot with two points, one obtained from an earlier kinetic run (Report Four, Fig. 7). The two points could possibly represent a leveling off, as shown in Curve C. However, the zero value obtained at 120 seconds refutes this. Time limitations prevented us from running a kinetic plot with more points from 20 to 1% unreacted material. Figure 8 shows an extrapolation of the 14-second point, and predicting a zero value (0.01% starting material) at 30 seconds reaction time.

With two minutes as a "found" zero time for cellobiose, and a 3 times factor for the cellodextrins, a minimum time of 6 minutes should be satisfactory for the latter. In Table I we have given reaction times of 20 and 60 minutes, which represent a large excess over the theoretical minimum time.

3. Agreement of the data obtained for soluble systems with those obtained for polysaccharides in heterogeneous systems. The data obtained by

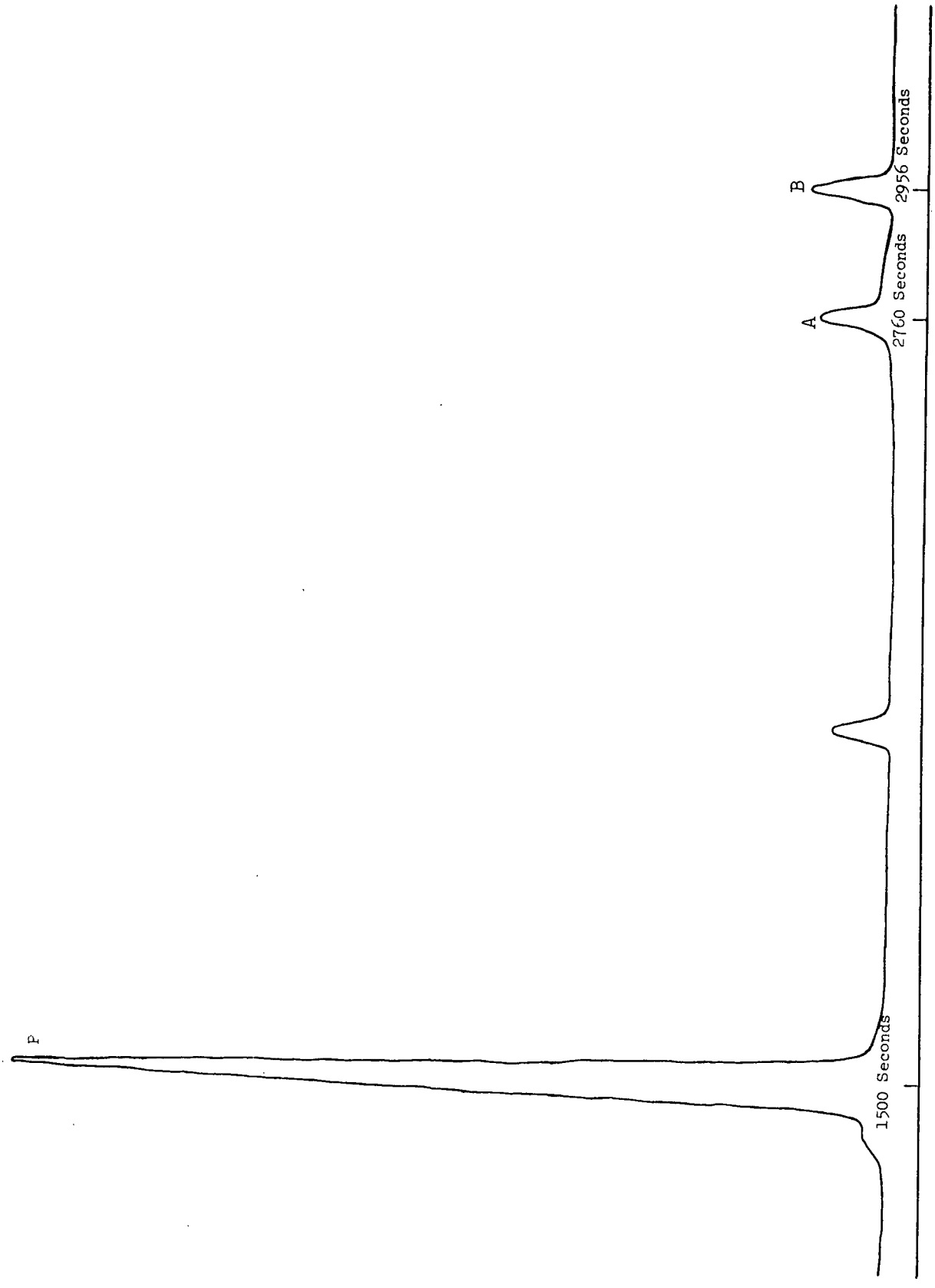

Figure 9. Unreacted Cellobiose, 14 Seconds in N NaOH at 120°C, Gas Chromatographic Curve, Trimethylsilyl Derivatives on OV-17 Column, 6 ft x 1/8 Inch, 130 to 250°C, at 2°/minute. Peaks A and B are α- and β-cellobiose and P is the Internal Standard,

Haas, et al. (1) have been discussed earlier, and it is reassuring that our values for a soluble system agree with those for a heterogeneous system.

4. Failure to show alkali-stable products by gas chromatography. Hopefully we should be able to show a small peak in the disaccharide or oligosaccharide regions, corresponding to 0.2% or less of the starting material. However, we have not been able to do this, and it may be a limitation of our technique of gas chromatography. At times we have obtained small peaks, but they approach the background noise of our recording system; also such small traces may be absorbed by the packings of our chromatographic columns. In a later section of this report, in our work with polysulfide systems, we were readily able to detect peaks of the order of 0.5%.

We have tried to reduce the background noise, or column bleed, in our gas chromatography by using a cold-injection technique. This involves injecting samples on the column beyond the injection port; the latter is unheated. The temperature of the column, in the oven portion only, is heated by a normal programming.

Also we have used a septum extender, to prevent overheating of the septum, and injecting into a heated injection block. Both methods have reduced background noise at the detector, but at present we have not detected repeatedly small peaks in the disaccharide region. Occasionally we have found small peaks but subsequent analyses of these (see below) has not been reassuring.

One other difficulty with our gas chromatography is that a very large sample of silylated material must be injected in order to find such small peaks. These samples, of the order of 5-10 microliters, lead to excessive fouling of the detector.

5. Analysis of the disaccharide region by thick paper chromatography. In order to obtain 1-2 mg of "disaccharide" material, we have spotted large samples (200-500 mg) of reaction products on Whatman 3 MM paper, and after development of the chromatogram, extracted the portion of the paper containing the disaccharide region (that where cellobiose would normally appear). In one case we obtained a small amount of material that, when trimethylsilylated and run on the gas chromatograph, gave a single peak in the disaccharide region. However, after hydrolysis this material gave only glucose as a product, and no metasaccharinic acid; both products were expected if the material were a stopping acid.

This experiment was repeated twice but the original results could not be confirmed and we assume the single disaccharide peak was an artifact. Control experiments, running a mixture of glucose and meta-saccharinic acid through the hydrolysis procedure, gave the expected peaks on the gas chromatograph.

One explanation of our failures in this area may be our assumption that a disaccharide acid will run at the same speed on a paper chromatogram as cellobiose. On the gas chromatograph such acids (based on data for cellobionic acid) should have retention times similar to those for cellobiose. It may be that behavior on paper is different.

6. Presence of trace amounts of oxygen in alkaline solutions. Control experiments with distilled water have shown that a procedure of alternate evacuation and flushing with nitrogen will reduce the oxygen concentration from 8.8 milligrams per liter to about 0.8 milligrams, or a removal of 90% of the dissolved oxygen. We have not run such determinations on our reaction solutions, but these have been carefully flushed with nitrogen as above. In some cases the alkali has been boiled to remove air before addition of carbohydrates.

The amounts of oxygen are relatively small. A solution of cellobiose (20 milligrams per milliliter) in alkali would contain 0.8 micrograms of oxygen per milliliter, or a weight ratio of 25,000 to 1. If we assume that one gram of cellobiose (molecular weight 342) reacts with 0.1 gram of oxygen (molecular weight 32), then the reaction ratio will be changed to 2,500 to 1. This is well below a value of 0.1%, and the amount of stopping we have determined is above this.

THE POLYSULFIDE STOPPING REACTION

BACKGROUND

The stopping reaction with sodium polysulfide is an oxidation of the reducing end unit, in contrast to the rearrangement observed in alkaline stopping. This oxidation is much faster, relative to peeling, than the alkaline stopping, and with cellobiose reactions in the present work the final reaction products contain appreciable amounts of disaccharide acids that can be readily detected by the gas chromatograph.

Aqueous sodium polysulfide solutions have a relatively low pH, of the order of 10.5, and have quite rapid oxidizing capacities. However, commercial pulping liquors usually consist of a mixture of sodium hydroxide and sodium polysulfide; such liquors are often made by the oxidation of white liquor (2), a mixture of sodium hydroxide and sodium sulfide. In such a reaction the alkalinity of the solution is increased.

$$2\ Na_2S + 1/2\ O_2 + H_2O \rightarrow Na_2S_2 + 2\ NaOH$$

Ahlgren, et al. (3) treated a hydrocellulose with an alkaline polysulfide solution at 100°C and hydrolyzed the product to give a variety of acidic units. These were mostly gluconic,-mannonic, and arabinonic acids; the arabinonic C_5 acid was predominant. In contrast Szabo and Teder (4) obtained a predominance of the gluconic and mannonic C_6 acids, and quite a bit of the erythronic C_4 acid. One can ascribe the gluconic acid to the direct oxidation of the glucose end unit, and the mannonic acid to either isomerization of the glucose unit before oxidation, or a slow isomerization of the gluconic acid after its formation. The C_5 and C_4 acids are probably formed by breaking of the double bond in the enediol form of the sugar units. Some of these reactions are shown in Fig. 10.

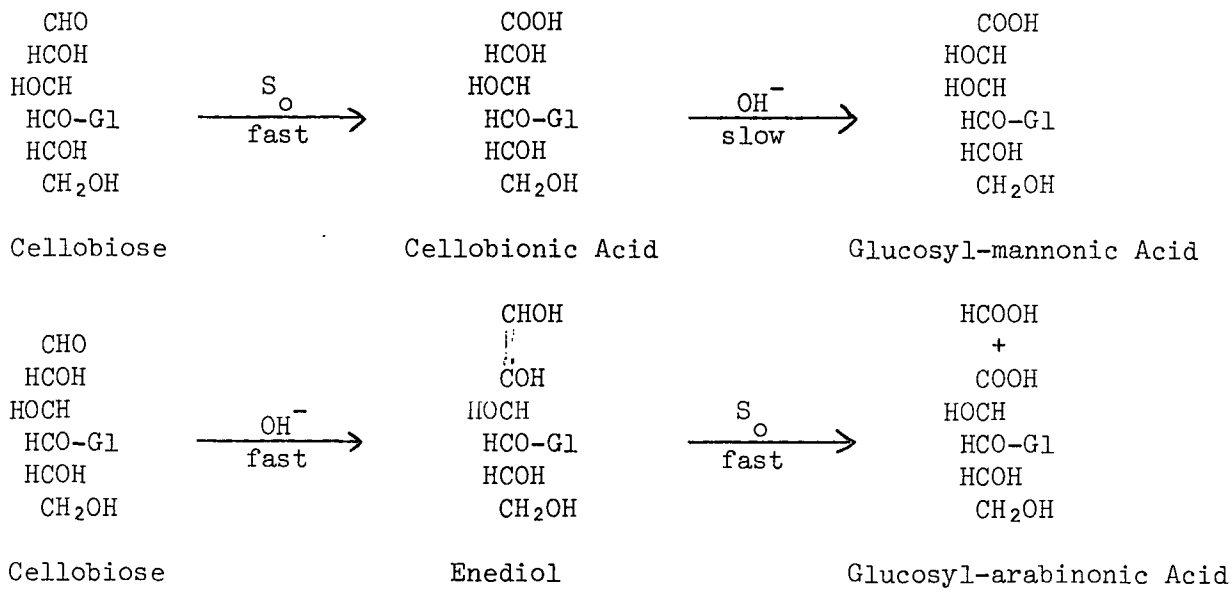

Figure 10. Oxidation of Cellobiose to C_{12} and C_{11} Acids

EXPERIMENTAL RESULTS

In the present work we have made no attempt to isolate the various acids by hydrolysis, but have determined the total amount of the disaccharide acids by gas chromatography. These peaks are readily detected, as two major and two minor peaks, and one of these (B) seems to slowly change with time into the other major peak (C). It is assumed that peak B is cellobionic acid and that it is slowly changing to glucosyl-mannonic acid. The other two peaks may be other disaccharide acids, or the four peaks may represent two acids and the lactones.

The gas chromatograms are shown in Fig. 11 and 12. The first figure shows the acids of earlier retention time, saccharinic acids and aldonic acids containing six carbon atoms or less. The second figure shows the four disaccharide peaks, of later retention time. There is an intermediate peak, between the disaccharide acids and the internal standard, which may be a disaccharide acid of lower carbon content.

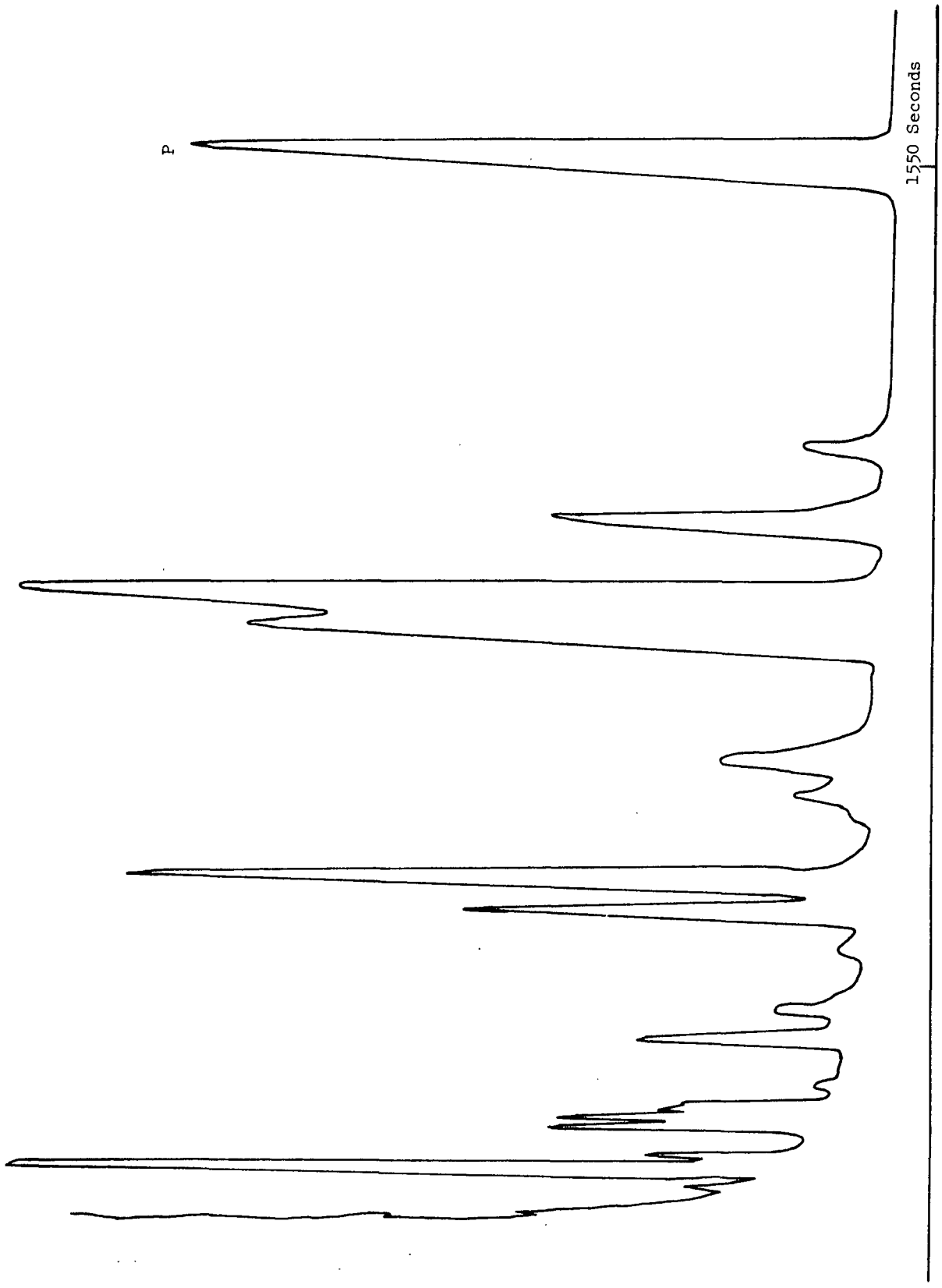

Figure 11. Typical Lower Molecular Weight Products from Reaction of Cellobiose and Orange Liquor, Trimethylsilyl Derivatives on OV-17 Column, 6 ft x 1/8 Inch, 130 to 250°C, at 2°/minute. Peak P is the Internal Standard and the Other Peaks

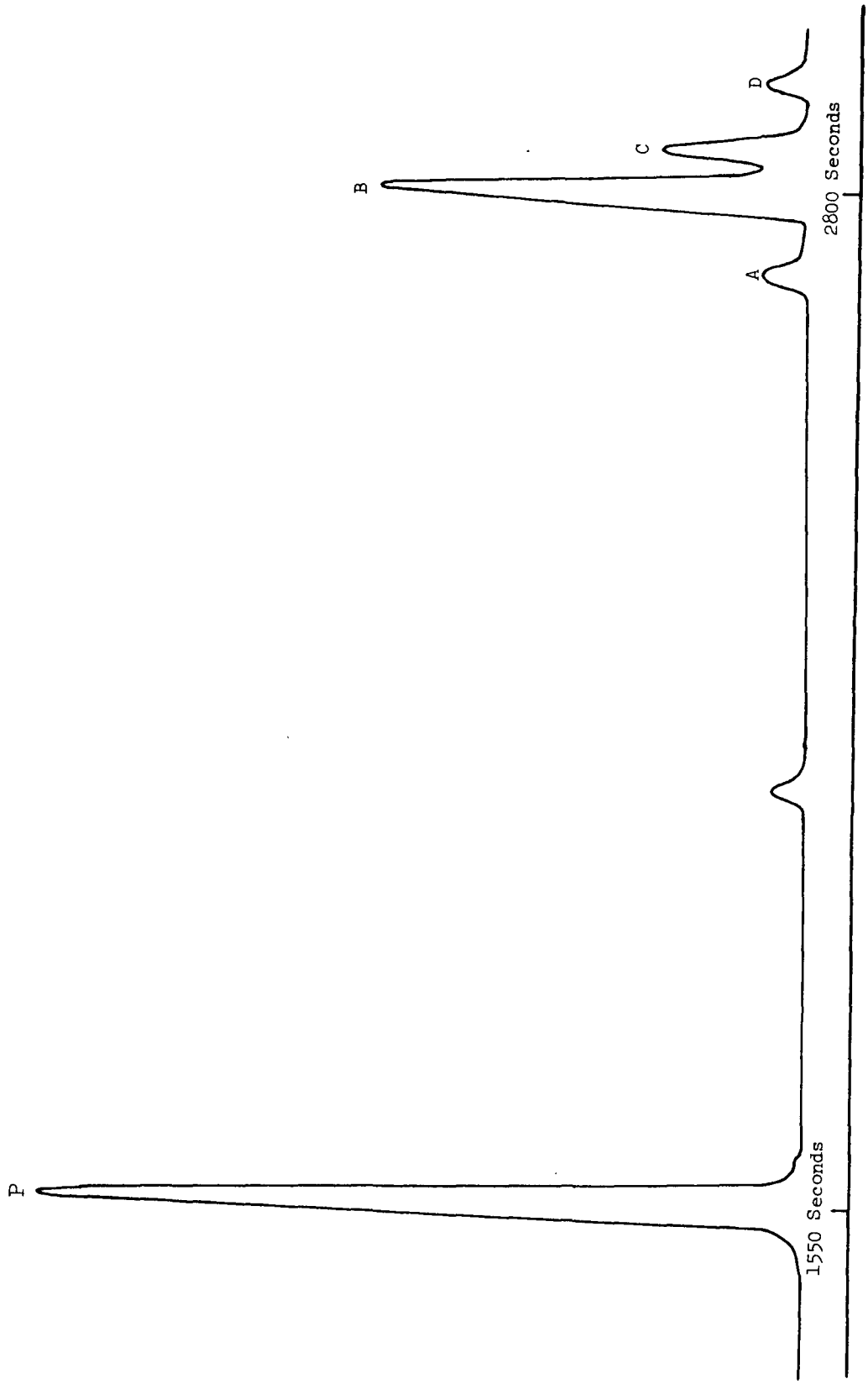

Figure 12. Disaccharide Acids Formed from Reaction of Cellobiose and Orange Liquor, Trimethylsilyl Derivatives on OV-17 Column, 6 ft x 1/8 Inch, 130 to 250°C, at 2°/minute. Peak P is the Internal Standard, Perseitol. (This Chromatogram is the Second Half of that Shown in Fig. 11.)

The yields of disaccharide acids and the conditions of their formation are shown in Table II. The total yield of the four peaks range from 4 to 8%; this yield is an estimate, as the response factor of these acids to the internal standard is not known. The yields are of the same order as that reported by Ahlgren, et al. (3) for a reaction at 100°C; their yield was determined by fractionation on a cellulose column.

The yields reach a maximum at 120°C; this may be because of the higher initial concentration of polysulfide at this temperature, in contrast to that at 150°C. Polysulfide is lost very rapidly at the higher temperature. Also at both temperatures there is a decrease in total yield after two minutes reaction time. The present work does not show whether this decrease is due to alkali alone or whether there is an oxidative degradation by the polysulfide.

The competitive effect of alkali (peeling) for the end units is shown in Table III. Cellobiose, when treated with sodium polysulfide solution alone (pH 10.5) gave a very high yield of disaccharide acids; when this solution was diluted with alkali, the yield dropped drastically. We cannot explain the lower yield of acids in the more dilute alkali; we had expected the yield to fall off directly with increase in alkali concentration. It may be that two effects are produced by the addition of alkali to a polysulfide solution — a negative effect of peeling and a positive effect in increasing the oxidizing action of the polysulfide. The latter effect is then appreciable only in the stronger alkali.

TABLE II

POLYSULFIDE STOPPING REACTION FOR CELLOBIOSE

Temp., °C	Time, min	Initial Liquor Composition,[a] g/l			Amount of Disaccharide Acids Formed[b]				
		NaOH	Na_2S	S_o	% A	% B	% C	% D	Total
90	60	79	19	7.75	0.58	2.22	0.58	0.60	3.96
120	15 sec	79	20	6.75	--	4.40	1.20	0.53	6.13
	2	79	20	6.75	0.55	5.45	1.45	0.71	8.15
	20	79	20	6.75	0.66	5.16	1.64	0.58	8.04
150	2	79	25.9	2.9	0.36	3.7	1.10	0.33	5.49
	20	79	25.9	2.9	0.37	2.4	1.8	0.26	4.86
100	240	31.4	12.5	10.4					7.0 approx.[c]

[a] The orange liquor composition is that resulting after 5 minutes in the heating coils at the given temperature, and then dilution with an equal volume of aqueous cellobiose solution (see Table IV). The NaOH concentration is the initial concentration, before heating, and decreases slightly with loss of polysulfide. The concentration of cellobiose, after mixing is 5 mg/ml. Yields of disaccharide acids are based on a 1:1 response factor with the internal standard, perseitol.

[b] This is only an estimate; if the acids have the same response factor toward perseitol as does cellobiose, then each value should be multiplied by 1.4.

[c] See Ref. (3) for this work.

TABLE III

RELATION OF PEELING AND STOPPING IN POLYSULFIDE SOLUTIONS

Solution	Composition, g/l NaOH	Na_2S	S_o	Temp., °C	Time, hr	Total Yield Disaccharide Acids
A	0	76.8	123.5	90	1	48.5
C	32	12.5	20.7	90	1	8.8
D	8	12.5	20.7	90	1	3.4

THERMAL STABILITY OF POLYSULFIDE IN ORANGE LIQUOR

Olsson and Samuelson (5) have given plots of the decomposition of sodium polysulfide solutions at various temperatures, and also for various concentrations of sodium hydroxide. Samples were taken at intervals of one to twenty-four hours. Decomposition of polysulfide solution alone is negligible at 90°C, but is very rapid at 155°C (85% decomposition in one hour). Data for varying amounts of sodium hydroxide added were done only at 100°C; the rate of decomposition was accelerated about five times in 1 to 2N sodium hydroxide. Thus, one would predict that orange liquor, at 150°C, would be almost completely decomposed in ten minutes.

Data for such thermal decomposition are given in Table IV. It can be seen that loss of polysulfide is much greater at 150°C than at 120°C. Also the loss in polysulfide was accompanied by a partial increase in sulfide content. According to Olsson and Samuelson the polysulfide reacts with alkali to form both sulfide and thiosulfate.

$$4\ S + 6\ NaOH \rightarrow 2\ Na_2S + Na_2S_2O_3 + 3\ H_2O$$

The data in Table IV are for orange liquor of twice the normal concentration; this liquor was used in the flow reactor and diluted with an equal volume of aqueous cellobiose solution. The data obtained at 5 minutes were used, with the dilution factor, for the initial concentrations given in Table II.

TABLE IV

THERMAL STABILITY OF SODIUM POLYSULFIDE

Temp., °C	Time, min	Sodium Sulfide, g/l	Elementary Sulfur, g/l
120	0	38	15.52
	5	40	13.5
150	0	39.2	13.6
	5	51.8	5.8
	10	54.2	1.7

Note — The initial concentration of sodium hydroxide in the orange liquor was 158 g/l. No analyses were run for NaOH. The concentrations of this liquor are high, as in the flow reactor it is diluted with an equal volume of cellobiose solution.

EXPERIMENTAL PROCEDURES

ALKALINE STOPPING REACTIONS

The runs at 90°C were made in a round bottom glass flask, with a glass stopper equipped with a stopcock. The alkali and carbohydrate were added to the flask, and the solution subjected to alternate evacuation and flushing with nitrogen to remove any dissolved air. This procedure was repeated five times. A magnetic stirring bar was placed in the bottom of the flask to facilitate solution of the carbohydrate; the cellobiose dissolved readily but the cellodextrin dissolved slowly in the cold alkali.

The flask, containing a nitrogen atmosphere, was then placed in the oil bath for a given period of time, removed and cooled. An internal standard was added at this stage; the amount was generally 1/10th of the weight of the original carbohydrate. It has been found that often these standards (inositol and perseitol) are not completely stable in the alkaline solutions.

The solution was then treated with Amberlite IR-120 resin to remove sodium ion, and the filtrate (pH about 3) concentrated for subsequent silylation or acid hydrolysis.

In these experiments the amount of carbohydrate ranged from 8 to 20 milligrams per milliliter. The alkali was always in great excess relative to the carbohydrate.

The runs at 120°C were made in the flow reactor. The alkali was boiled first, then cooled. For experiments with cellobiose, the carbohydrate was dissolved in a given volume of water, and this solution and the alkali drawn into the two reaction syringes. The heating and reaction coils were

pressurized (see Report Four for this operation), the oil bath raised to cover the heating coils. The latter were heated for five minutes, and then the cellobiose and alkali were driven into the heating coils and allowed to equilibrate for five minutes. Then the two solutions were mixed and allowed to react for a given period of time. The reaction was stopped by mixing the reaction solution with dilute acetic acid to a pH of about 4. The quenched solution was then treated with IR-120 resin to remove sodium ion, the filtrate concentrated in vacuo to dryness to remove acetic acid and worked up for analysis.

In experiments with cellodextrins in the flow reactor at 120°C, the cellodextrin has to be dissolved in cold alkali before the start of the reaction; it is not soluble in cold water. Hence, solutions of the cellodextrin in alkali and alkali of equal strength are run into the heating coils in the oil bath, maintained for five minutes, and then mixed for a given period of time before quenching. Based on work with thermocouples, the cellodextrin solution should be up to temperature in 1-2 minutes; heat transfer through the metal heating coils is very rapid. However, this heat up time is indefinite, so that no kinetic experiments for short periods of time can be run. Hence, the reaction times for the cellodextrins are the sum of time in the heating coils and time in the reaction coil.

POLYSULFIDE STOPPING REACTIONS

The reactions at 90°C were run in the same manner as those cited for the alkaline stopping reactions, in glass flasks for a given period of time. The solutions were then cooled, IR-120 resin added to remove sodium ion and nitrogen bubbled through for one hour to remove hydrogen sulfide. The mixture of resin and precipitated sulfur was then removed, and the filtrate worked up.

Reactions at 120 and 150°C in the flow reactor were run by mixing aqueous solutions of cellobiose and of orange liquor, after first bringing them to temperature in the heating coils. No runs were made with polysulfide solutions and cellodextrins. The reactions were stopped by quenching with dilute acetic acid, to a pH of about 4-5 (see Fig. 13-14). The nitrogen pressure on the flow reactor was relieved with venting of hydrogen sulfide fumes into a hood. The quenched solution was treated with IR-120 resin and worked up as above.

REMOVAL OF COLLOIDAL SULFUR FROM ACIDIFIED POLYSULFIDE SOLUTIONS

Concentration of the filtrate, following removal of ion-exchange resin and precipitated sulfur, gives a yellow-white residue which contains appreciable amounts of sulfur. This sulfur is dispersed colloidally in the original filtrate and is removed only with difficulty. The best method, we have found, is to dissolve the residue in 1-2 ml of water, centrifuge the solution to remove undissolved sulfur, and concentrate the supernatant liquid. The new residue still contains some sulfur, and so the process of solution and centrifugation is repeated. After about five such operations the final residue is a sirup, which contains very little sulfur. This can then be trimethylsilylated for analysis by gas chromatography.

STABILITY OF POLYSULFIDE SOLUTIONS

Portions of orange liquor were introduced into a reaction syringe, the flow reactor pressurized and the heating coils brought to temperature (120 or 150°C) during a period of ten minutes. The orange liquor was then pushed into one heating coil and water into the other coil. After five minutes the two solutions were mixed and rapidly pushed through the reaction coil and quenched

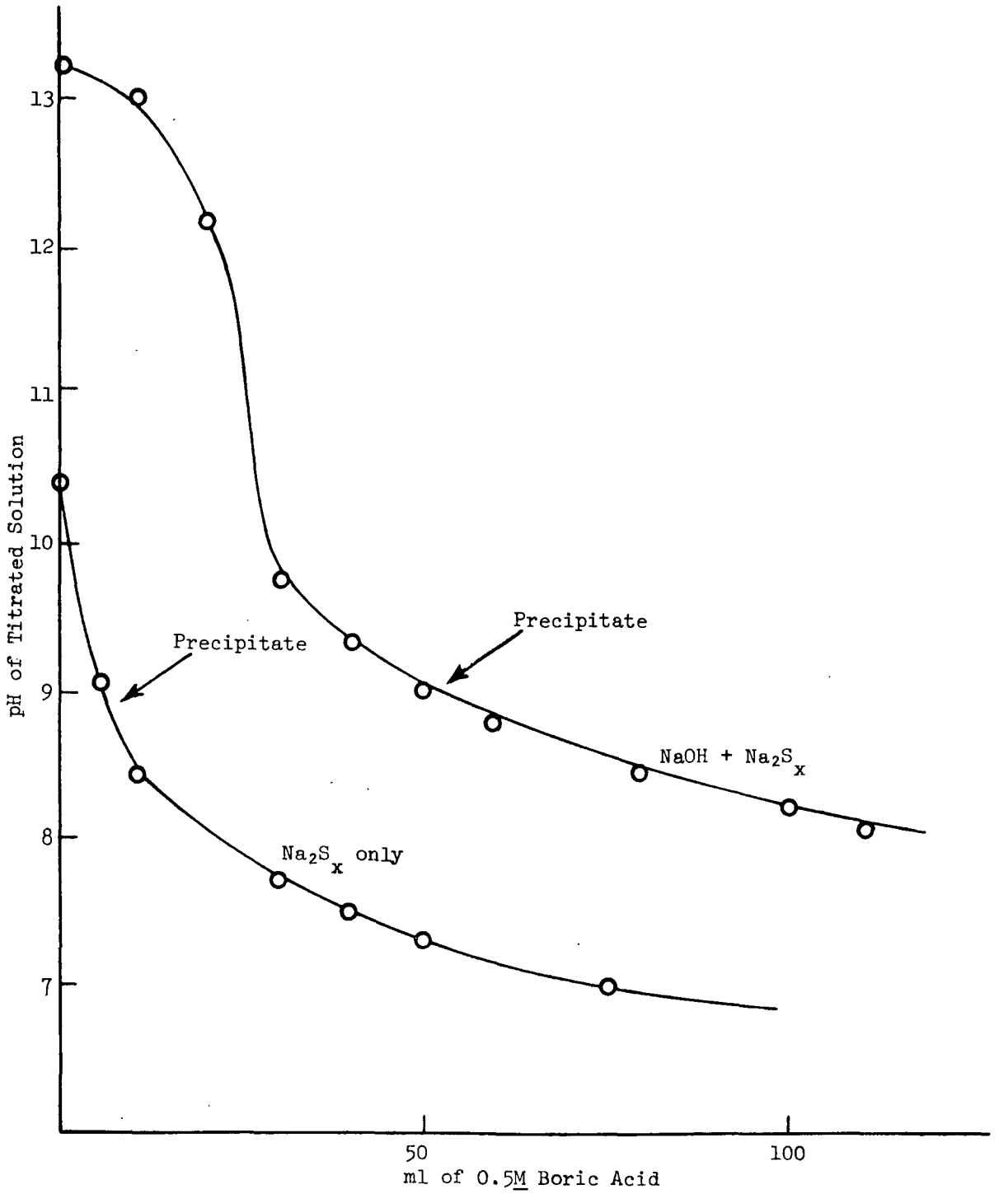

Figure 13. Quenching of Polysulfide Solutions with Boric Acid

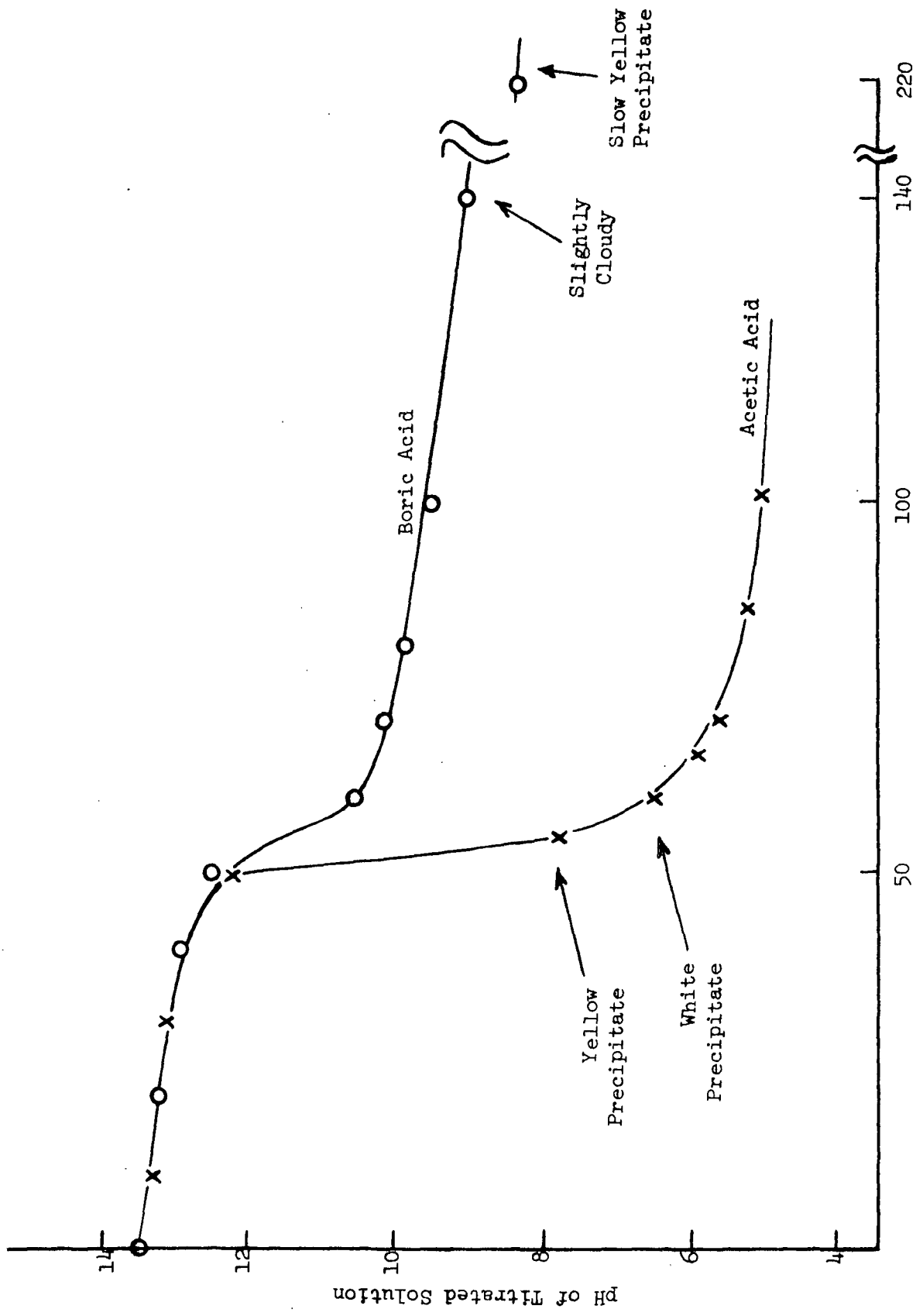

Figure 14. Quenching of Orange Liquor with Different Acids

by addition of cold water. The cold solution was analyzed for sulfide and free sulfur and allowance made for dilution of the original solution.

OPERATION OF THE FLOW REACTOR

Most of the operations of the flow reactor at 120 and 150°C were of the intermittent type; this is discussed in detail in Report Five, page 40. The total volume of the two heating coils and the reaction coil was about 35 ml; of the 41.6 ml of solution pushed from the reaction syringes into the system, about 6.6 ml of liquid passed the second mixer and was washed with the quench liquid into the quench bottle. This volume of reaction solution recovered was determined by pushing alkali of a certain concentration through the system, at a given temperature and pressure, and titrating the quenched solution.

The above volume of 6.6 ml was found for alkaline solutions. For solutions containing sulfide, we found slightly less, about 5.8 ml. There is a definite expansion of liquid in the heating and reaction coils, and this expanded liquid is pushed out of the system by cold liquid from the reaction syringes. Hence, the expanded liquid contracts, and the total volume removed does not seem to vary appreciably with temperature. Tests run with sodium polysulfide solution at 90°C showed an expansion about 50% greater than for water.

GAS CHROMATOGRAPHY

The various samples were converted to the trimethylsilyl derivatives, as described in earlier reports. Two internal standards were used, inositol and perseitol. The latter is a 7-carbon straight chain polyhydric alcohol, (6) and has a slower retention time than inositol. It has been used in the

determination of cellobiose and the disaccharide acids obtained in polysulfide reactions. Inositol was used in quantitative determinations of glucose found by hydrolysis of stopping reactions; this compound was used in earlier experiments reported in Report Six. Both standards were added in most cases after the alkaline reactions; they are not completely stable in the hot alkaline systems.

The internal standards were added in a ratio of 1/10th the weight of the original carbohydrate. This means that when we are looking for a product of the order of 1% of the original reactant, the ratio of this product to the internal standard will be of the order of one to ten, and the ratio of peak areas can be easily handled. However, it also means that a large amount of material is injected on the gas chromatograph; most of this is saccharinic acids of six carbons or below. Injection of such large amounts (5-10 microliters) of silylated material tends to overload the chromatographic column and foul up the detector. Only in the case of glucose hydrolyzates, where the acidic material is removed by MB-3 resin and only the glucose and inositol remain, is this problem of overloading avoided.

To avoid this injection of large amounts of material, we have tried to operate the gas chromatograph at a high sensitivity. This results in a poor base line, due to either bleeding of the column or bleeding of the septum (high injection temperatures). Two approaches were made to this problem. The first was to use a cold injection chamber, and inject samples through the chamber directly on the portion of the column in the oven. This required a hypodermic syringe with a 5-inch needle; a good base line was obtained but it was not easy to operate the syringe; the latter was a 50-microliter gas-tight Hamilton needle; the gas-tight feature was needed to force liquid through the long needle. A good base line was obtained with this technique.

The second approach was to use a septum extender, a fitting that extended the septum one inch from the heated injection chamber. This also gave a good base line and was much easier to use than the cold injection technique. Satisfactory chromatograms were obtained with samples of mono- and disaccharides.

The cold injection technique, while not being used at present, might be more applicable for mixtures of oligosaccharides. The absence of a hot injection port, and the gradual increase in temperature of the oven containing the chromatographic column, might be beneficial.

PREPARATION OF POLYSULFIDE SOLUTIONS

A sodium polysulfide solution (A) was made up by solution of Na_2S-9 H_2O in water, then addition of powdered sulfur and stirring for 30 minutes. The mixture was filtered from undissolved sulfur, and the filtrate analyzed; found 76.8 g/l of Na_2S (61.1 g/l as Na_2O) and 123.5 g of elementary sulfur (S_o). The solution was stored under kerosene to prevent access of air.

Portions (8.1 ml) of this solution were diluted with water and 2N NaOH to 50 ml to give two alkaline solutions:

C, 12.5 g/l Na_2S, 20.7 g/l S_o and 0.8N NaOH

D, 12.5 g/l Na_2S, 20.7 g/l S_o and 0.2N NaOH

An orange liquor was made up for reactions in the flow reactor; this was 4N in NaOH, and contained 38 g/l Na_2S and 15.5 g/l elementary sulfur. It was mixed with equal volumes of cellobiose solution in the flow reactor so the original concentrations were cut in half. It was also diluted similarly with cellobiose solution for a batch reaction at 90°C.

CHEMICAL ANALYSIS OF POLYSULFIDE SOLUTIONS

The sulfide content was determined by potentiometric titrations of aliquots with 0.1N $AgNO_3$; the titrations were monitored with an Orion sulfide ion specific electrode Model 94-16A and an Orion double junction reference electrode Model-90-02. The polysulfide content was calculated from the increase in sulfide content after reduction of an aliquot with sodium amalgam (7).

In all cases a portion of the solution was diluted to ten volumes, and a 10-ml aliquot taken. It was transferred to a 400-ml beaker, 100 ml 5% NH_4OH (or 10 ml of concentrated NH_4OH) and one spoonful (about 2 grams) of Na_2SO_3 were added, and the titration made. The end point occurs when the readings drop 100-200 millivolts with addition of 0.1 ml of 0.1N $AgNO_3$ solution.

For the determination of polysulfide, the 10 ml aliquot was stirred with 15 ml of sodium amalgam for one minute longer than the time required to decolorize the solution. The aqueous phase was rinsed from the amalgam with 150-200 ml water into another beaker. Concentrated NH_4OH (5 ml) and several grams of Na_2SO_3 were added, and the solution titrated with 0.1N $AgNO_3$, as above. The increase in sulfide content is the polysulfide (S_o) content of the aliquot.

The sodium amalgam was made by electrolysis of 100-200 grams of mercury in 200 ml saturated sodium carbonate solution for 4 hours at 4-6 amperes. The anode was placed in the carbonate solution and the cathode in the mercury. The amalgam was used several times to reduce polysulfide solutions, and was discarded when a greenish black precipitate formed in the reducing step.

IDEAS FOR FUTURE WORK

This report marks the closing of Project 2942, but there are several avenues of work that could be considered, if further interest in this area is maintained. Some of these ideas will be explored on Project 3265, a Funded Project on Alkali-Oxygen Reactions (especially items 3 and 4 below). Also we wish to remind the reader that during the course of Project 2942 we have developed a flow reactor that can be used to explore various rapid reactions up to a temperature of 170°C and at reaction times as short as 10 milliseconds. This equipment will be available if some of the member mills wish to utilize it for individual or group problems.

1. Effect of alkali on the oxidative capacity of polysulfide solutions. This has just been briefly touched on in the present report, and solutions of constant polysulfide content and varying alkali concentration and pH could be utilized with carbohydrate substrates.

2. The effect of polysulfide solutions on soluble lignin systems. The products could be examined for degree of oxidation by a wet-oxidation method, such as the iodic acid method of Kleinert, where the consumption of oxidant is related to the carbon dioxide evolved.

3. A further investigation of the stopping reaction with alkali alone. Improved techniques will be applied to isolate the stopping acids. High pressure liquid chromatography can be utilized, and also methods of injecting large samples on the gas chromatograph.

4. Fractionation of mixtures of oligosaccharides by high pressure liquid chromatography. The present mixtures used in this project were not completely soluble in water, and a preliminary fractionation of these mixtures with water and dilute alkali will be utilized.

ACKNOWLEDGMENTS

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